

**Early strength water reducing agent for non-alkali concrete**

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**Abstract of CN 1099089 (A)**

The non-alkali efficient water reducer is made up of naphthalene through sulfuric acid sulfonation, formaldehyde condensation and lime neutralization, as well as mixing with ordinary water reducer, hydrated silicate minerals, inorganic salt of non-alkali metal, organic strength promoter, etc. grinding and mixing. As alkali is removed, long service life of concrete is ensured.

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[57] 摘要

本发明涉及一种无碱混凝土用早强减水剂,属建筑材料技术领域。该无碱早强减水剂是由羧基硫酸磺化、甲醛缩合、石灰中和后制成的无碱高效减水剂,再与普通减水剂、硅酸盐水合矿物、非碱金属无机盐、有机促强剂及硅灰等其它辅料经一定配比,磨碎、混合而成。本发明研制的减水剂除去了已有减水剂中的碱类物质,因而保证混凝土有足够长的使用寿命。

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## 权 利 要 求 书

1、一种无碱混凝土用早强减水剂, 其特征在于早强减水剂由下列各组分组成:

(1) 无碱高效减水剂, 其制备工艺为: 将苯经硫酸磺化, 磺化的比例为苯: 硫酸=1: 0.5~1.5, 磺化温度为125℃~180℃, 时间为2~5小时, 然后经甲醛缩合, 缩合比例为: 苯: 甲醛=1: 0.5~1.5, 缩合时间为3~8小时, 缩合温度为85℃~120℃, 最后用石灰中和至中性, 经过滤干燥制得;

(2) 非碱金属无机盐, 为硫酸钙、硝酸钙、硫酸镁或硝酸镁中的任何一种, 由市售得到;

(3) 硅酸盐水合矿物, 为 $3\text{MgO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ ,  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$ ,  $6\text{MgO} \cdot 4\text{SiO}_2$ ,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$ 中的任何一种, 将其经干燥、破碎、粉磨至80~100目即可使用;

(4) 有机促强剂, 为三异丙醇胺, 三乙醇胺, 甲醇, 乙酸钙, 甲酸钙和尿素中的任何一种, 其制备方法为将上述液体的1: 1~10 的比例与粉煤灰混匀成粉体, 粉碎至过80目筛;

(5) 辅料, 为粉煤灰、硅灰和沸石粉中的任何一种, 粉碎至过80目筛; 将上述五种组分与市售普通减水剂以下列比例混合均匀, 即成产品:

无碱高效减水剂: 2~10%

普通减水剂: 0.5~5%

非碱金属无机盐: 5~30%

硅酸盐水合矿物: 10~80%

有机促强剂: 0.05~0.5%

辅料: 适量

# 说明书

## 无碱混凝土用早强减水剂

本发明涉及一种无碱混凝土用早强减水剂，属建筑材料技术领域。

混凝土在有一定湿度、一定碱含量及骨料(或集料)有活性的条件下，会产生碱·骨料反应，产生膨胀，破坏混凝土，使其导致开裂以至完全丧失功能，因而有混凝土中癌症之称。目前水泥中碱含量(以 $\text{Na}_2\text{O}$ 计)已接近产生碱·骨料反应临界值( $1.8\sim 3.8\text{kg/m}^3$ )，一般在 $2.5\sim 3.5\text{kg/m}^3$ 左右，存在着产生碱·骨料反应危险。现在广泛在混凝土中使用着早强减水剂估计全国每年达几万吨。而这些早强减水剂绝大多数含大量碱类物质。如常用的以元明粉为主的早强减水剂，在掺量3%、水泥用量 $300\text{kg/m}^3$ 的条件下，会引入混凝土中 $3.9\text{kg/m}^3$ 的碱类。由于它们均为易溶盐类，更易参加反应。因此，这些外加剂加入到混凝土中，只要其它条件具备，肯定会大大促进产生此类有重大危害作用的碱·骨料反应。

本发明的目的是研制一种无碱混凝土用早强减水剂，除去已有技术所用早强减水剂中的碱类物质，以保证混凝土有足够长的使用寿命。

本发明的内容是：

无碱混凝土用早强减水剂，由下列各组分组成：

(1) 无碱高效减水剂，其制备工艺为：将萘经硫酸磺化，磺化的比例为萘：硫酸=1：0.5~1.5，磺化温度为 $125^\circ\text{C}\sim 180^\circ\text{C}$ ，时间为2~5小时。然后经甲醛缩合，缩合比例为萘：甲醛=1：0.5~1.5，缩合时间为3~8小时，缩合温度为 $85\sim 120^\circ\text{C}$ ，最后用石灰中和至中性，经过滤干燥制得。

(2) 非碱金属无机盐，为硫酸钙、亚硝酸钙、硝酸钙、硫酸镁或硝酸镁中的任何一种，由市售得到。

(3) 硅酸盐水合矿物，为 $3\text{MgO}\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$ ， $\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\cdot\text{H}_2\text{O}$ ， $6\text{MgO}\cdot 4\text{SiO}_2$ ， $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaSO}_4\cdot 12\text{H}_2\text{O}$ 中的任何一种。将其经干燥、

破碎、粉磨至80~100目即可使用。该类水合矿物可以是某种天然水合硅酸盐矿物，也可以由人工合成制得。

(4) 有机促强剂，为三异丙醇胺，三乙醇胺，甲醇，乙酸钙，甲酸钙和尿素中的任何一种。其制备方法是将上述液体品以1:1~10的比例与粉煤灰混匀成粉体，粉碎至过80目筛。若为固体品，可直接将其粉碎至过80目筛使用。

(5) 辅料，为粉煤灰、硅灰和沸石粉中的任何一种，粉碎至过80目筛。将上述五种组分与市售普通减水剂以下列比例混合均匀，即成产品：

无碱高效减水剂：2~10%	普通减水剂：0.5~5%
非碱金属无机盐：5~30%	硅酸盐水合矿物：10~80%
有机促强剂：0.05~0.5%	辅料：适量

下面介绍本发明的几个实施例。

#### 实施例一

苯1kg，加0.8kg硫酸，在125℃磺化3小时，加入0.8kg甲醛在85℃下缩合5小时，加水2kg，加石灰乳适量，使其 $\text{PH}=7.5\sim 8.0$ ，过滤、干燥、粉磨至通过80目筛成产品；加入木素磺酸钙0.5kg；加入磨细至80目的硫酸钙10kg；加入硅酸盐水合矿物 $3\text{MgO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ 磨细至80目的粉末20kg；加入有机促强剂甲酸钙2.5kg；（磨细至80目），混合均匀成产品。

#### 实施例二

苯1kg，加1.2kg浓硫酸，在150℃磺化3小时，加入0.8kg甲醛缩合，在95℃下缩合4小时，加水2kg，加石灰乳使 $\text{PH}=7\sim 8$ ，过滤、干燥、粉磨至通过80目筛成产品；加入普通减水剂木素磺酸钙0.3kg；加入磨细至80目的亚硝酸钙15kg；加入 $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$ 磨细成80目的粉末

30kg; 加入磨细至通过80目的甲酸钙4kg; 混匀成产品。

### 实施例三

萘1kg, 加1.5kg硫酸, 在170℃磺化5小时, 加水0.3kg, 加甲醛0.9kg, 在110℃缩合4小时, 再加水2kg, 加石灰乳中和至 $\text{PH}=7.5\sim 8.5$ , 过滤、干燥、粉磨至通过80目; 加入木素磺酸钙1.5kg; 硝酸镁10kg; 磨细至80目的  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$  20 kg; 加入1份甲醇与10份粉煤灰拌匀物0.5kg; 混匀成产品。

## **An alkali-free early strength water reducer used in concrete**

### **Specification**

The present invention, in the field of constructional materials, relates to an alkali-free early strength water reducer used in concrete.

Under the conditions of certain humidity, certain alkali content and aggregate being active, a reaction between alkali and aggregate may take place in concrete to cause expansion, thereby destroying concrete to make it crack till completely losing its function. At present, cement has an alkali content (counted by  $\text{Na}_2\text{O}$ , generally in the range of about  $2.5\text{--}3.5 \text{ kg/m}^3$ ) approximating to the critical value ( $1.8\text{--}3.8 \text{ kg/m}^3$ ) at which the reaction between alkali and aggregate may take place, and is in the risk of causing the reaction between alkali and aggregate. Currently, early strength water reducers are widely used in concrete at an amount of up to tens of thousands tons per year. However, an absolute majority of these early strength water reducers contain a lot of alkali substances. Taking a common early strength water reducer primarily containing anhydrous sodium sulfate as an example, when its amount is 3%, and the amount of cement is  $300 \text{ kg/m}^3$ ,  $3.3 \text{ kg/m}^3$  alkali substances may be introduced to concrete. As being soluble salts, these substances are much prone to take part in the reaction. Thus, only if other conditions are provided, when these additives are added to concrete, they will certainly promote to a great extent the proceeding of said highly harmful reaction between alkali and aggregate.

The object of the present invention is to develop an alkali-free early strength water reducer used in concrete, which is free of alkali substances that are used in the present early strength water reducers, thereby assuring concrete to have enough long service life.

### **Contents of the Invention**

An alkali-free early strength water reducer used in concrete comprises:

- (1) An alkali-free high efficiency water reducer, prepared by the steps of:  
sulfonating naphthalene with sulfuric acid at a ratio of naphthalene/sulfuric acid

= 1:0.5-1.5 and a temperature of 125-180°C for 2-5 h; condensing the resulting product with formaldehyde at a ratio of naphthalene/formaldehyde = 1:0.5-1.5 and a temperature of 85-120°C for 3-8 h; and finally neutralizing the system with lime till neutral followed by filtering and drying.

(2) A non-alkali metal inorganic salt, which is any one of calcium sulfate, calcium nitrite, calcium nitrate, magnesium sulfate and magnesium nitrate, and which is commercially available.

(3) A silicate hydrated mineral, which is any one of  $3\text{MgO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ ,  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$ ,  $6\text{MgO} \cdot 4\text{SiO}_2$ , and  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$ , which is dried, crushed and milled to a particle size of 80 to 100 meshes prior to use. This kind of hydrated mineral may be natural or synthetic hydrated silicate mineral.

(4) An organic strengthening agent, which is any one of tri-isopropanolamine, triethanolamine, methanol, calcium acetate, calcium formate and urea, prepared by mixing the above substance in liquid state with fly ash in a ratio of 1:1-10 to obtain a powder, and then crushing the powder to a particle size of exceeding 80 meshes. If the substance is in solid state, it may be directly crushed to a particle size of passing through 80 mesh sieve prior to use.

(5) An adjuvant, which is any one of fly ash, wollastonite, and zeolite powder, which is crushed to a particle size of passing through 80 mesh sieve.

The product of interest is prepared by mixing the above five components with a commercially available common water reducer in the following ratios:

An alkali-free high efficiency water reducer: 2-10%

A common water reducer: 0.5-5%

A non-alkali metal inorganic salt: 5-30%

A silicate hydrated mineral: 10-80%

An organic strengthening agent: 0.05-0.5%

An adjuvant: q.s.

## Examples

### Example 1

1 kg naphthalene was sulfonated with 0.8 kg sulfuric acid at 125°C for 3 h, and then condensed with 0.8 kg formaldehyde at 85°C for 5 h; 2 kg water was



added to the system followed by adequate lime cream to obtain a pH = 7.5-8.0; after filtering and drying, the resulting product was milled to a particle size of exceeding 80 meshes; to which 0.5 kg calcium lignosulfonate, 10 kg calcium sulfate having a particle size of 80 meshes, 20 kg of a silicate hydrated mineral  $3\text{MgO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$  having a particle size of 80 meshes, and 2.5 kg of an organic strengthening agent calcium formate having a particle size of 80 meshes were added followed by mixing to obtain the product.

#### Example 2

1 kg naphthalene was sulfonated with 1.2 kg sulfuric acid at  $150^\circ\text{C}$  for 3 h, and then condensed with 0.8 kg formaldehyde at  $95^\circ\text{C}$  for 4 h; 2 kg water was added to the system followed by adequate lime cream to obtain a pH = 7-8; after filtering and drying, the resulting product was milled to a particle size of passing through 80 mesh sieve; to which 0.3 kg of a common water reducer calcium lignosulfonate, 15 kg calcium nitrite having a particle size of 80 meshes, 30 kg  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$  having a particle size of exceeding 80 meshes, and 4 kg of calcium formate having a particle size of 80 meshes were added followed by mixing to obtain the product.

#### Example 3

1 kg naphthalene was sulfonated with 1.5 kg sulfuric acid at  $170^\circ\text{C}$  for 5 h, and then condensed with 0.9 kg formaldehyde after adding 0.3 kg water at  $110^\circ\text{C}$  for 4 h; 2 kg water was further added to the system followed by adequate lime cream to obtain a pH = 7.5-8.5; after filtering and drying, the resulting product was milled to a particle size of passing through 80 mesh sieve; to which 1.5 kg of calcium lignosulfonate, 10 kg magnesium nitrate, 20 kg  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$  having a particle size of 80 meshes, and 0.5 kg of an admixture of 1 parts methanol and 10 parts fly ash were added followed by mixing to obtain the produ

## Claims

1. An alkali-free early strength water reducer used in concrete, which is characterized by comprising:

(1) an alkali-free high efficiency water reducer, prepared by the steps of: sulfonating naphthalene with sulfuric acid at a ratio of naphthalene/sulfuric acid = 1:0.5-1.5 and a temperature of 125-180°C for 2-5 h; condensing the resulting product with formaldehyde at a ratio of naphthalene/formaldehyde = 1:0.5-1.5 and a temperature of 85-120°C for 3-8 h; and finally neutralizing the system with lime till neutral followed by filtering and drying;

(2) a non-alkali metal inorganic salt, which is any one of calcium sulfate, calcium nitrate, magnesium sulfate and magnesium nitrate, and which is commercially available;

(3) a silicate hydrated mineral, which is any one of  $3\text{MgO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ ,  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$ ,  $6\text{MgO} \cdot 4\text{SiO}_2$ , and  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$ , which is dried, crushed and milled to a particle size of 80 to 100 meshes prior to use;

(4) an organic strengthening agent, which is any one of tri-isopropanolamine, triethanolamine, methanol, calcium acetate, calcium formate and urea, prepared by mixing the above substance in liquid state with fly ash in a ratio of 1:1-10 to obtain a powder, and then crushing the powder to a particle size of passing through 80 mesh sieve; and

(5) an adjuvant, which is any one of fly ash, wollastonite, and zeolite powder, and which is crushed to a particle size of passing through 80 mesh sieve;

the above five components are mixed with a commercially available common water reducer in the following ratios:

an alkali-free high efficiency water reducer: 2-10%

a common water reducer: 0.5-5%

a non-alkali metal inorganic salt: 5-30%

a silicate hydrated mineral: 10-80%

an organic strengthening agent: 0.05-0.5%

an adjuvant: q.s. to obtain the product.

## Abstract

The present invention, in the field of constructional materials, relates to an alkali-free early strength water reducer used in concrete. The alkali-free early strength water reducer is prepared by the steps of: sulfonating naphthalene with sulfuric acid; condensing it with formaldehyde, and neutralizing with lime to obtain an alkali-free high efficiency water reducer; then, milling and mixing the alkali-free high efficiency water reducer with a common water reducer, a silicate hydrated mineral, a non-alkali metal inorganic salt, an organic strengthening agent and an adjuvant such as wollastonite in certain ratios. The present alkali-free early strength water reducer is free of alkali substances that are used in the present early strength water reducers, thereby assuring concrete to have enough long service life.